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CA 2096835 C 2001/10/23
(11)(21) 2 096 835
(12) BREVET CANADIEN
CANADIAN PATENT
(13) C

(22) Date de dépôt/Filing Date: 1993/05/21
(41) Mise à la disp. pub./Open to Public Insp.: 1994/11/22
(45) Date de délivrance/Issue Date: 2001/10/23

(51) Cl.Int.^{5}/Int.Cl.^{5} C10M 139/00, C10M 129/26

(72) Inventeurs/Inventors:
Bhatnagar, Akhilesh K., IN;
Rai, Madan M., IN;
Naithani, Kanta P., IN;
Verma, Amar S., IN;
Sayanna, Eltepu, IN;
Kumar, Anoop, IN

(73) Propriétaire/Owner:
Indian Oil Corporation Limited, IN

(74) Agent: RIDOUT & MAYBEE

(54) Titre : COMPOSITION DE GRAISSE LUBRIFIANTE
(54) Title: LUBRICATING GREASE COMPOSITION

(57) Abrégé/Abstract:
Lubricating grease compositions based on titanium complex soap thickener in mineral and synthetic base oils have been prepared for the first time. Tentative methods for preparing lubricating grease from this new type of titanium complex soap thickener have been described. High performance lubricating grease resulted from titanium terphthalate stearate complex soap thickener, exhibited excellent mechanical stability, high drop point, excellent oxidation stability, very good extreme pressure and antiwear properties, good water resistance and corrosion inhibiting characteristics.

ABSTRACT OF DISCLOSURE

Lubricating grease compositions based on titanium complex soap thickener in mineral and synthetic base oils have been prepared for the first time. Tentative methods for preparing lubricating grease from this new type of titanium complex soap thickener have been described. High performance lubricating grease resulted from titanium terphthalate stearate complex soap thickener, exhibited excellent mechanical stability, high drop point, excellent oxidation stability, very good extreme pressure and antiwear properties, good water resistance and corrosion inhibiting characteristics.

BACK GROUND OF INVENTION:

FIELD OF INVENTION:

This invention relates to the development of high performance lubricating grease composition based on completely new type of titanium complex soap thickeners viz., Titanium terephthalate stearate. Titanium metal component in complex soap thickener has been derived from titanium isopropoxide rather than an alkali. Several carboxylic acid and fatty acid combinations with titanium isopropoxide have been tried in order to get a lubricating grease of comparable performance characteristics with other high performance lubricating grease as lithium complex, aluminum complex, sulfonate complex or polyurea greases. Best emerged combination, terephthalate stearate complex soap in mineral base stock exhibited, if not better, comparable performance characteristics to other above mentioned high performance lubricating greases.

PRIOR ART

In the prior art, metallic soaps and their complex soaps have generally been used as thickeners in lubricating grease industry. The continuous large scale usage of these type of thickeners in grease formulations is perhaps due to their excellent thickening capacity, easy availability and cost factors. Most of these commercially applicable metallic or complex metallic soap thickeners are derived from metals such as lithium, calcium, sodium, barium, aluminium etc., and are well known in the art.
With few exceptions, metallic soaps other than mentioned previously constitute minor portion of thickeners in lubricating greases. In fact, in most cases soaps of miscellaneous metals serve some functions other than that of thickeners.
However, in early stage C.J. Boner in Ind. Eng.Chem. 29,59(1937) have mentioned the preparation of soaps of Cd,Ce,Mg,Cr,Co,Hg,Sn in an attempt to prepare lubricating grease. Nevertheless in course of time these soaps have not gained commercial significance in lubricating greases.

Similarly, U.S. Patent No.2878236 describes titanium stearate used as polymerisation catalyst. Another indication (Klarkes Markley's fatty acid part-II, Inc.NY 1961,P.717) on titanium stearate provided the melting point of titanium sterate soap as 62°C. Therefore, perhaps because of low melting point of these titanium soaps have not been used as thickeners in lubricating greases. Complex soaps of titanium, however, have not been reported so far for lubricating grease purpose.

In commercial formulations of lithium and calcium complex soap base greases,metallic compound used for their preparation are the oxides/hydroxides of respective metals. On the other hand, in aluminium complex soap base grease,metallic component is derived from aluminium isopropoxide in place of an alkali (NLGI July 1965) and these greases are gaining increased commercial applications. Interestingly, alkoxide/isopropxide of several other metals are also well known in prior art (Bradley, D.C.et.al in "Progress in Ing.Chem.Vol.II Interscience P.303 (1960), J.Chem.Soc,2027 1952 and 2025, 1953). In recent years reactive alkoxides of titanium are commercially available at attractive prices. This is because of wide spread abundancy of Ti metal in earth crust (The Wealth of India, Industrial Products Part VIII CSIR,1973). Fully substituted alkoxides of titanium are prepared by melles process. Reaction of monohydric alcohol with titanium tetrachloride is carried out in an inert solvent which may be a hydrocarbon or a chlorinated hydrocarbon and in presence of hydrochloric acid acceptor, such as sodium metal, ammonia and certain amines (US Patent No.2187,721(1940), Brit., Patent No. 512452 (1939).

It was found interesting to note hereinto that majority of soap or complex soap thickeners of commercial significance for formulating lubricating greases are either metals derived from alkali or alkaline earth metals. However metallic soap thickeners from transition metal elements for formulating lubricating greases have hitherto not attracted attention by the inventors. Nevertheless exploring the possibility of making complex soap thickeners for high performance lubricating greases from this new class of metal derivatives could be of great scientific significance. Keeping this view in mind, extensive attempts have been made to prepare complex soap thickener from titanium alkoxides with different combinations of carboxylic acids and fatty acids to put knife in the heart of wonder.

OBJECTS OF THE INVENTION

A primary object of this invention is to propose a novel lubricating grease composition capable of use as lubricant for automotive and industrial applications.

Another object of this invention is to propose a novel lubricating grease composition having suitable mechanical and oxidation stability properties.

Still another object of this invention is to propose a novel lubricating grease composition having a high drop point and good EP and antiwear properties.

Yet another object of this invention is to propose a novel lubricating grease composition having good water resistance and corrosion inhibition characteristics.

A further object of this invention is to propose a process for the preparation of lubricating grease compositions having the aforesaid properties.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with this invention the lubricating grease composition comprises 2 to 20% by weight of titanium alkoxide, 2 to 20% by weight of carboxylic acid, 5.0 to 35.0% by weight of fatty acids, 0.0 to 5.0% by weight of water and 20 to 90% by weight of mineral/synthetic oil.

In accordance with a preferred embodiment of this invention the lubricating grease composition 2 to 20% by weight of titanium alkoxide, 5 to 25% by weight of fatty acid, 2 to 20% by weight of carboxylic acid, 0.0 to 5.0% by weight of water and 20 to 90% by weight of mineral/synthetic oil.

Further according to this invention, there is provided a process for the preparation of a lubricating grease composition which comprises by forming in the first stage a mix by adding together fatty acid, carboxylic acid and mineral or synthetic oil in required proportions, stirring and heating such a mix to a temperature of 70 to 100°C, adding in the second stage titanium dioxide in the required proportions while maintaining said temperature, raising the temperature to 100° to 200°C to form a thickened grease product, cooling said product, and in the third stage adding water thereto, if required, and then subjecting the mixture to the step of shearing.

In accordance with this invention, a vessel equipped with a stirrer of rpm 0-150 in the first stage, is charged with 5 to 35% by weight of fatty acid, 2 to 20% by weight of carboxylic acid and 20 to 90% by weight of mineral or synthetic oil, based on the total weight of the final grease composition.

The mixture is stirred and heat is provided through a heating mantle to reach the temperature to 70-100°C. At the end of the first stage, 2 to 20% by weight of titanium alkoxide is added slowly based on the total weight of the final grease composition.

The mixture is continuously mixed and held at 70-100°C for 1-2 hours, temperature being raised very slowly to 100-200°C, duration of maintaining at this temperature is 2-8 hours. During this period the product assumes grease structure and converts to a thickened mass. The product is then cooled with continuous stirring to 140-100°C at the end of this second stage, if desired up to 5% by weight of water is added to the mixture, based on the total weight of the final grease composition. The mixture is further cooled to 80-60°C and sheared with the help of a colloid mill. The resulting product of NLGI No. 1 to 5 is obtained.

It is, however, possible to combine the first and second stages to provide an alternate route.

Thus, according to this invention there is provided an alternate process for the preparation of a lubricating grease composition which comprises in preparing in the first stage a mix by adding together fatty acid, carboxylic acid, titanium alkoxide and mineral or synthetic oil in required proportions, heating such a mixture to a temperature of 160 to 200°C, cooling the resultant mix and in the second stage adding required water thereto, stirring the cooled mix and then further cooling said mix and subjecting it to the step of shearing.

In accordance with the alternate process of this invention, the charge is stirred with simultaneous heating through a heating mantle. The mixture is heated upto a temperature of 160-200°C in 2-8 hours. The resultant product is cooled to 140-80°C and water is added from 0.1 to 5.0%. This is further stirred for 5 minutes to 1 hour at this temperature and then further cooled to 80-50°C and sheared in a colloid mill. The resultant product of NLGI NO.1-5 is obtained.

Titanium alkoxides used in present invention is preferably titanium alkoxide of C3 to C6 alcohol having titanium metal content of 17% by weight approximately and used in the amount 2-20% by weight of the final lubricating grease composition. The synthetic hydrocarbon lubricating oil used in the compositions of present invention are an oligomer of olefin such as polyalpha olefins, polybutenes, polyehteres, mineral base stocks are the neutral oils.

The sources of fatty acids employed in the grease compositions are alkyl carboxylic acids from vegetable sources which may have few double bonds in the structure. For instance, it includes stearic acid, hydroxystearic acid, oleic acid, mahuwa oil, etc. This is present in amount of 5 to 35% by weight of the final lubricating grease composition.

The carboxylic acids employed in this invention are, for example, mono-carboxylic acid ranging from acetic acid to BVC acid, C2 to C10 carbon chain dicarboxylic acids, hydroxydicarboxylic acids such as tartaric acid and citric acid, aromatic acids include mono and dicarboxylic acids both, as well as hydroxy mono carboxylic acid , for example, benzoic acid, salicylic acid, phthalic acid, terepthalic acid, (Table I). Inclusion of inorganic acids like boric and phosphoric is also the illustration of present invention. This is present in amount 2.0 to 20% by weight of the final lubricating greases.

In order to describe more fully the nature of the present invention, specific examples will hereinafter be described. It should be understood, however, that this is done solely by way of example and is intended neither to delineate nor limit the ambit of the appended claims.

EXAMPLE NO. 1

The lubricating grease composition has been prepared consisting the ingredients with proportions indicated as described hereinbelow. and following the procedure as indicated above. Here fatty acid used is stearic acid 5.6% and titanium alkoxide is titanium tetraisopropoxide, 6.6%. Table No. 1 demonstrates the various carboxylic acids 6.6% tried with a view of preparing lubricating grease.

Table No.1

Carboxylic acids used in the inventions

S.No.	Carboxylic acid	Structure
1.	Acetic acid	CH_3COOH
2.	B.V.C. acid	$CH_3(CH_2)_nCOOH$
3.	Oxalic acid	$(COOH)_2$
4.	Malonic acid	$CH_2(COOH)_2$
5.	Succinic acid	$(CH_2)_2(COOH)_2$
6.	Glutaric acid	$(CH)_3(COOH)_2$
7.	Azelaic acid	$(CH_2)_7(COOH)_2$
8.	Sebacic acid	$(CH_2)_8(COOH)_2$
9.	Tartaric acid	[CH(OH)COOH]
10.	Citric acid	CH_2COOH $C(OH)COOH$ CH_2COOH
11.	Benzoic acid	C_6H_5COOH
12.	Salicylic acid	$C_6H_4(CH)COOH$
13.	Phthalic acid (ortho benzene dicarboxylic acid)	$C_6H_4(COOH)_2$
14.	Terephthalic acid (para benzene dicarboxylic acid)	$C_6H_4(COOH)_2$
15.	Fumaric acid	$(CH\ COOH)_2$
16.	Maleic acid	$(CH\ COOH)_2$
17.	Cinnamicacid	$C_6H_5CH{=}CH{-}COOH$

Table No. 2 represents few physico chemical test data of some of the greases.

TABLE NO. 2

S.NO.	CARBOXYLIC ACID USED	TOTAL FATTY MATERIAL IN % IN MINERAL OIL	DROP POINT D-566/ D-2265 C	WORKED PENETRAT AT 25 C D-217
1.	GREASE NSA (Succinic Acid)	27.2	232	305
2.	GREASE TTA (Tartaric Acid)	28.6	220	281
3.	GREASE CTA (Citric Acid0	30.8	215	278
4.	GREASE PTA (Phthalic Acid)	25.4	250	181
5.	GREASE TPA (Terephthalic Acid)	14.6	296	281

EXAMPLE No. 2

The lubricating grease composition has been preepared by the method of Example No. 1 by adding 5.6 of commercially available titanium isopropoxide 6.6% of phthalic acid, 5.6% of stearic acid, the remainder being mineral base oil and water.

Lubricating grease was prepared by the method described above. Lubricating grease thus prepared exhibited physico - chemical characteristics indicated in Table-3.

TABLE NO. 3

S. NO.		ASTM/IP METHOD	RESULTS
1.	PENETRATION AT 25° C AFTER 60 STROKES	D - 217	230
2.	DROP POINT °C	D - 566	249
3.	COPPER CORROSION AT 100 C AFTER 24 HRS	TP-112	PASS
4.	RUST PREVENTIVE PROPERTIES	D - 1743	PASS
5.	WATER WASHOUT % Wt.	D - 1264	1.9
6.	ROLL STABILITY % CHANGE 2 HRS.	D - 1831	8.0
7.	FOUR BALL BP TEST WELD LOAD KG.	IP - 239	160
8.	FOUR BALL WEAR TEST 40 KG, 75 C 1200 RPM & 1 HR WEAR SCAR DIA MM	D - 2266	0.6

The effectiveness of the lubricating grease composition described above demonstrates its high drop point, good shear stability, good corrosion resistance, good chemical stability and good EP and antiwear properties.

EXAMPLE NO.3

This example has a variation as synthetic hydrocarbon oil (PAO) was used in place of mineral oil, otherwise all other conditions and ingredients are the same as stated in Example No.2.

The resultant grease exhibited the following physico-chemical characteristics as indicated in Table No.4.

TABLE NO. 4

S.NO.	PROPERTY	TEST RESULTS
1.	PENETRATION AT 25 °C 60 STROKES	278
2.	DROP POINT °C	262
3.	COPPER CORROSION	PASS
4.	RUST PREVENTIVE PROPERTIES	PASS
5.	WATER WASHOUT % WT.	2.0

This example has demonstrated improved drop point, and good water resistance and good corrosion inhibition properties.

EXAMPLE NO.4

This example illustrates the preparation of lubricating grease with ingredients in the proportions as indicated in Example No.2 hereinabove. The polycarboxylic acid used is terephthalic acid and other ingredients are the same as titanium isopropoxide, stearic acid, mineral base oil and water.

The lubricating grease prepared as per described method and ingredients without any performance additive exhibited following physicochemical characteristics in Table No.5.

TABLE NO.5

S.No.	PROPERTY	ASTM/IP METHOD	RESULTS
1.	MECHANICAL STABILITY AT 25C		
	AJ WORKED PENETRATION	D-217	254
	BJ AFTER 100000 STROKES		271
	CJ CHANGE FROM 60 STROKES		+15 UNIT
2.	DROP POINT °C	D-566	258
3.	OXIDATION STABILITY	D-942	
	AJ AFTER 100 HRS		1 PSI DROP
	BJ AFTER 500 HRS		5 PSI DROP
4.	WATER WASHOUT	D-1264	1.9%
5.	LOSS ON EVAPORATION	D-972	0.6%
6.	COPPER CORROSION AT 100 C +/-5 C,24 HRS	IP 112	PASS
7.	LOW TEMP.TORQUE AT - 30C	IP 186	
	AJ STARTING		3500 gmcm
	BJ RUNNING		500 gmcm
8.	FOUR BALL EP TEST WELD LOAD KG	IP-239	280
9.	FOUR BALL WEAR TEST 40 KG, AT 15 C, 1200 ROM, 1 HR WEAT SCAR DIA,MM.	D-2266	0.4 MM

The effectiveness of the lubricating grease composition descrit :d above demonstrates its high drop point, excellent shear stability, good corrosion resistance, excellent EP and antiwear properties, excellent oxidation stability which fulfils the objective to be a high performance lubricating grease capable of commercial applications.

EXAMPLE NO.5

This example illustrates the preparation of lubricating grease with proportions indicated in **Example 1.** The polycarboxylic acid used is terephthalic acid, monocarboxylic acid is stearic acid, titanium alkoxide is titanium isopropoxide, mineral oil and water. The lubricating grease prepared as per the alternate method described earlier exhibited the following physico-chemical characteristics as indicated in Table-6. In this alternate process, all ingredients in known quantities are taken simultaneously.

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S. NO.	PROPERTY	ASTM/IP METHOD	RESULT
1.	PENETRATION AT 25 ^{o}C AFTER 60 STROKES	D - 217	295
2.	DROP POINT ^{o}C	D - 2265	296
3.	COPPER CORROSION AT 100 ^{o}C , 24 HRS	IP 112	PASS
4.	WATER WASHOUT % Wt	D - 1264	2.0

This alternate process for making lubricating grease has shown enhanced drop point, good shear stability, good corrosion resistance and improved water resistance properties.

EXAMPLE NO. 6

The lubricating grease composition has been prepared consisting the ingredients with the proportions indicated below.

The lubricating grease composition consists of 11.3% of commercial titanium, isopropoxide, 6.6% of teraphthalic acid, 11.3% of oleic acid, the remainder being mineral base oil and water.

The composition prepared as per example No. 2 has the following characteristics as shown in Table - 7.

TABLE NO. 7

S. NO.	PROPERTY	ASTM/IP METHOD	RESULT
1.	PENETRATION AT 25° C AFTER 60 STROKES	D - 217	139
2.	DROP POINT °C	D - 556	248
3.	COPPER CORROSION AT 100 C. 24 HRS	IP 112	PASS
4.	WATER WASHOUT % Wt.	D - 1264	2.0

The effectiveness of the lubricating grease with oleic acid in place of stearic acid has shown good thickening capacity and shear stability while maintaining high drop point, good water resistance and good corrosion resistance characteristics.

CLAIMS:

1. A lubricating grease composition comprising 2 to 20% by weight of titanium alkoxide, 2 to 20% by weight of carboxylic acids other than fatty acids, 5.0 to 35.0% by weight of fatty acids, 0.0 to 5.0% by weight of water and 20 to 90% by weight of an oil selected from the group consisting of mineral and synthetic oils.

2. A lubricating grease composition as claimed in claim 1 wherein the said oil is an oligomer of olefin selected from the group consisting of polyalpha olefin, polybutene and polyethers, said carboxylic acids selected from the group consisting of acetic acid, b.v.c. acid, oxalic acid, malonic acid, succinic acid, glutaric acid, azelic acid, sebacic acid, tartaric acid, citric acid, benzoic acid, salicylic acid, phthalic acid, terephthalic acid, fumaric acid, maleic acid and cinnamic acid, said fatty acids being selected from the group consisting of oleic acid and stearic acid.

3. A lubricating grease composition as claimed in claim 1, wherein the alkoxide is titanium alkoxide of C3 to C6 alcohol having titanium metal content of approximately 17% by weight.

4. A lubricating grease composition as claimed in claim 1 where fatty acid is mahuaw oil.

5. A process for the preparation of a lubricating grease composition which comprises by forming in a first stage a mix by adding together fatty acid, carboxylic acid other than fatty acid and mineral or synthetic oil, stirring and heating such a mix to a temperature of 70° to 100° C., adding in a second stage titanium dioxide while maintaining said temperature, raising the temperature to 100° to 200° C. to form a thickened grease product, cooling said product and in a third stage optionally adding water thereto and then subjecting the mixture to the step of shearing.

6. A process as claimed in claim 5 wherein 2 to 20% of titanium alkoxide is added.

7. A process as claimed in claim 5 wherein the mixture in the first stage is continuously mixed and held at 70°-100° C. for 1-2 hours and in the second stage at a temperature of 100° to 200° C. for a period of 2 to 8 hours.

8. A process as claimed in claim 5 wherein the mix is cooled with continuous stirring to 140°-100° C. and 0-5% by wt. of water is added.

9. A process for the preparation of a lubricating grease composition, comprising preparing in a first stage a mix by adding together fatty acid, carboxylic acid other than fatty acid, titanium alkoxide and mineral or synthetic oil in required proportions, heating such a mixture to a temperature of 160° to 200°C., cooling the resultant mix and in a second stage adding required water thereto, stirring the cooled mix and then further cooling said mix and subjecting it to a step of shearing.

10. A process as claim in claim 9 wherein said mixture is cooled to a temperature of 140° to 80° C. in 2 to 8 hours.

RIDOUT & MAYBEE
Toronto, Canada
Patent Agents